ENERGETIC CONDENSATION GROWTH OF MgB_2 THIN-FILMS FOR SRF APPLICATIONS*

M. Krishnan, B. Bures, K. Wilson Elliott, Alameda Applied Science Corporation (AASC), San Leandro, California 94577, USA
J. Jiang, A. Gurevich, D.C. Larbalestier, Applied Superconductivity Center, National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, USA
A.-M. Valente-Feliciano, L. Phillips and C. Reece, Thomas Jefferson National Accelerator Facility (Jefferson Lab), Newport News, Virginia 23606, USA

Abstract

We report single-step vacuum growth of stoichiometric superconducting thin films of MgB_2, using AASC's cathodic arc deposition process. Energetic condensation using cathodic arcs produces non-equilibrium fast ions (~50-100eV) that allow growth modes on relatively low temperature substrates. We have demonstrated MgB_2 films with T_c of 34K by depositing at 275 °C *in a single step*, from a stoichiometric, *solid* MgB_2 source. In a subsequent experiment, the single-step coated samples (on c-plane sapphire) were sealed into small stainless steel containers prior to ex-situ annealing, to create a small volume that would quickly achieve a high partial pressure of Mg vapor upon heating to minimize loss of Mg from the films. Post-deposition anneal steps varied in temperature from 825–900K with duration of 15 minutes. This annealed films also showed a transition at 30K. Subsequently, an MgB_2 film was successfully deposited over a 50mm diameter circular area on a 63mm Buffered Chemically Polished (BCP) Niobium substrate for future RF evaluation in a cavity. The depositions spanned a range of substrate temperatures from 550-675 K. The films began to change in appearance form silver to black as substrate temperature was increased, indicating a decrease in magnesium content in the films. Future plans are to reduce oxygen contamination and to use our filtered cathodic arc to deposit smoother films.

INTRODUCTION

Most RF particle accelerators worldwide utilize RF cavities made from a conventional conductor such as copper to accelerate the particle beam. A few large research accelerators such as the Continuous Electron Beam Accelerator Facility (CEBAF) at Thomas Jefferson National Accelerator Facility (Jefferson Lab, or JLab) and the Spallation Neutron Source (SNS) use superconducting radio frequency (SRF) accelerating cavities. SRF cavities consume less power than conventional cavities to produce a given accelerating gradient, even when the additional energy cost of the cryogenics system is taken into account.[1,2] However the cryogenics system costs do represent a significant portion of the operating expense of SRF accelerators. Operation at higher temperature would naturally reduce those costs. Niobium, the only presently accepted superconductor for SRF accelerators, has a transition temperature T_c of 9.3K, but a practical operating temperature of 2K at the typically used 1.3–1.5 GHz RF frequencies. Operation below T_c is required to minimize surface resistance and maximize critical magnetic field. The cavities are typically made of niobium metal which becomes superconducting when cooled to a few degrees above absolute zero. Increasing the operating temperature of the accelerator from 2K to 4.5K could cut the cryogenics system costs in half [1,2] but would require use of an alternative superconductor with an operating temperature of 10K or higher. Since the RF (London) penetration depth on the cavity surface is only ~30nm, it is of interest to develop thin film coatings on the nano-scale (~100nm) for particle accelerators. Pioneering work [3-5] on Cu cavities coated with Nb thin film has been done at the European Organization for Nuclear Research, known as CERN. By 1998, 272 copper 352 MHz cavities, Nb thin film coated via magnetron sputtering, were deployed for the Large Electron-Positron Collider (LEP) project. The circular LEP collider, with a circumference of 27 kilometers, was one of the largest particle accelerators ever constructed and has recently been replaced by the Large Hadron Collider (LHC). Future accelerator facilities, such as the proposed International Linear Collider (ILC), require high accelerating field ~35 MV/m and $Q \geq 10^{10}$. It was reported [5,6] that at 1.7K the Nb thin film cavities for LEP had Q-drop to below 10^{10} at ≈15MV/m and to below 5×10^9 at ≈20 MV/m. Thus there is a motivation to better understand these limits and to improve Nb thin films' performance for future SRF accelerator cavities. There is also strong motivation to understand and develop SRF cavities with higher temperature superconductors, including the A-15 candidates [7,8].

In a recent article in Nature, Eric Hand [9] states that the superconducting cavities that drive most of the world's particle accelerators are running out of room for improvement. But new theoretical work suggests that overlooked superconducting materials could be used to make cavities that accelerate particles to higher energies over shorter distances - thereby doing the job more cheaply. Still, it would take years to develop and test new accelerator components made of materials such as triniobium tin. For decades, researchers have worked to improve the performance of superconducting cavities.

After more than 40 years of SRF research, there isn't a clear replacement for Nb. At first glance, MgB_2 (T_c~40K) appears to be a good candidate. However MgB_2 superconductivity was discovered only in 2001 by

Nagamatsu *et al* [10] so its RF properties are not as well characterized as those of Nb or other potential replacement superconductors such as Nb_3Sn. Furthermore MgB_2 is brittle when fabricated from a powder through sintering or hot isostatic pressing (HIP) – the two preferred methods for fabricating MgB_2 structures. Due to its brittleness, formation and mechanical tuning of a bulk MgB_2 cavity would be impractical. Coating tunable structures made of Nb or Cu with a thin film of MgB_2 appears to be the only approach to taking advantage of MgB_2 as a superconductor for SRF accelerators.

Catelani and Sethna [11] assert that the peak gradient for triniobium tin is 120 MeV/m and MgB_2 could reach 200 MeV/m. These gradients are to be contrasted with the best measured fields of about 60MeV/m in single Nb cavities. In practice, multiple cavities such as are required for a large accelerator are limited today, to fields ~20MeV/m. Thus the promise of an order-of-magnitude higher field in an MgB_2 cavity is tantalizing. Although a distant goal, achieving such gradients could result in huge savings for future accelerators. For example, the US$7-billion International Linear Collider (ILC) will use thousands of cavities, stretching along a tunnel 31 km long, to help it produce energies of 500 GeV. To do this, the ILC's Nb cavities must reach challenging gradients of >30 MeV/m. Ramping up the gradients to a theoretically possible peak of 200 MeV/m (in MgB_2) could significantly reduce the length of the ILC, therefore also reducing the costs of most of its physical parts such as tunnels and beam-lines.

There is a second approach to reducing SRF accelerator costs: to replace the expensive, bulk Nb (~$300/lb) cavities with a Nb thin film deposited on a less expensive material, such as Cu (~$3/lb) or better yet, Al (~$1/lb). The added advantage of Al over Cu is that the cavity can be cast instead of being machined, which is more expensive.

The payoff of higher temperature SRF cavities and cavities made out of thin-film coated Cu or Al has motivated a multi-year research program at Alameda Applied Sciences Corporation (AASC).

EXPERIMENTAL CONFIGURATION

Two thin-film coating chambers are at use at AASC, as shown schematically in Figs. 1 and 2. The experimental configuration for the CED™ chamber is shown in Fig. 1.

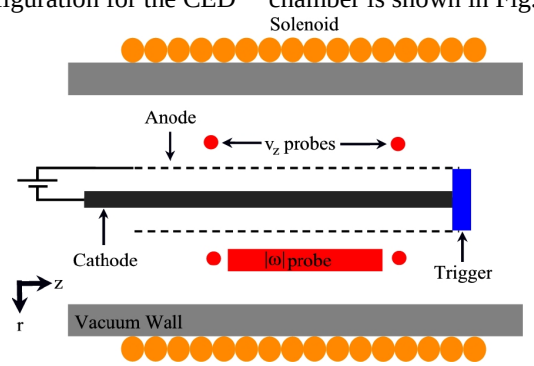

Figure 1: Illustration of the CED™ system.

The arc is formed between an on-axis cathode (1-cm diameter and 60-cm long) and a mesh anode (45-cm in length) at 1-cm radius. The arc is sustained by a PowerTen, Inc. power supply (100V, 200A). The repetition rate of the arc is 0.5Hz, limited at present by SCR switches, but may be increased by using IGBT switches to more rapidly turn off the arc between pulses. The arc is triggered by a proprietary trigger system. The substrate is placed outside the anode. The entire assembly is enclosed in a 25-cm dia. CF vacuum spool. The vacuum spool is double walled with a solenoid wound on the outside wall of the vacuum chamber. The solenoid is capable of producing a peak magnetic field of 10mT in either the z^+ or z^- direction.

The arc current is controlled by adjusting a ballast resistor in series with the cathode. Figure 2 shows the direct cathodic arc deposition source. In this source, plasma from the source (shown as Nb3Sn in this example) impinges directly upon a heated substrate located a few cm above the cathode. The substrate assembly is also designed to allow pulsed biasing of the substrate as shown.

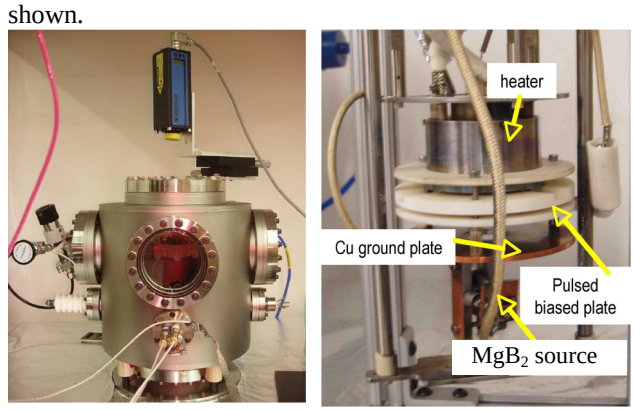

Figure 2: Photographs of the direct deposition cathodic arc system.

MgB_2 DEPOSITIONS

Deposition of MgB_2 utilizing both sources (Figs. 1 and 2) is now described. This work is believed to be the first attempt to utilize cathodic arc processes to deposit thin films of this material in a single step, without ex-situ annealing. The films were found to adhere well to A-plane and C-plane sapphire as well as to polished OFHC copper.

The Mg:B ratio in the film can be varied dramatically by heating the substrate. The substrate temperature was varied from 25-400 ºC which yielded films containing essentially no Mg at 400 °C to films of composition $MgB_{0.17}$ at 25 °C as determined by EDX. The EDX was calibrated against a measurement of sintered cathode material. Mg and B travel to the substrate from the MgB_2 cathode source as energetic ions. Since Mg and B vaporize at dramatically different temperatures, the transported material does not necessarily preserve the stoichiometry of source. When the substrate remains at room temperature, the sticking coefficients of both materials are large and the deposited thin films from an

MgB_2 source have a similar appearance to Mg thin films. Likewise room temperature (300K) deposition produces Mg rich films for PLD and magnetron sputtering from MgB_2 targets [12,13]. In the case of AASC's cathodic arc deposition, the ratio of Mg to B was 5:1 for room temperature deposition. To drive the Mg:B ratio to 1:2, substrate heating was required. With increasing temperature the sticking coefficient of Mg decreases more rapidly than that for B [14]. The sticking coefficient of Mg must change by 10 fold relative to that for B between 300 and 550 K. As the substrate was heated in excess of 550K, the films became B rich with respect to MgB_2. At 675K, Mg was absent from the films.

This strong relationship between substrate temperature and Mg sticking coefficient has driven the development of many annealing methods used in conjunction with other thin film deposition methods. As previously discussed, Mg rich films are deposited by PLD, magnetron sputtering and evaporation methods and then annealed *in-situ* to produce superconducting MgB_2. The excess Mg becomes the Mg vapor necessary to form superconducting MgB_2

Preferential removal of Mg from the cathode surface may cause the MgB_2 target to "age" over time as the surface becomes significantly Mg depleted. One possible way to compensate for this aging is to start with non-stoichiometric cathodes, which is easy to do as the cathodes are sintered from powdered mixtures.

Superconductivity in CED™ Deposited Films

Superconducting transitions were observed for several films deposited using CED™ with substrates heated to 250-275ºC. Fig. 3 shows the transitions (close to the ideal 38K value) measured in the raw MgB_2 cathodes as sintered. Transitions were observed at approximately 26K for films deposited at both 250ºC and 275ºC. The thickness of these films was measured to be approximately 1µm. One sample with approximately 2µm thickness deposited with a substrate temperature of 550K was shown to have T_c of 34K, see Fig. 4. The Mg:B ratio was very close to 1:2.

Film Thickness and Purity

Thickness measurements were made by profilometry. However, these depositions were performed with no macro-particle filtering and hence yielded films with RMS roughness several times greater than the film thickness. Hence the film thickness values quoted are approximate. The transitions observed were weak. Upon cooling the sample the resistivity dropped significantly at the transition temperature, but remained unacceptably high. This could be caused by insufficient connectivity between grains of MgB_2 as well as the presence of oxides in the films leading to resistance at the grain boundaries. No fundamental limit to film thickness was observed. Films as thick as 10 µm have routinely been deposited using our CED™ apparatus. The deposition of thicker MgB_2 films requires only an increase in the number of pulses during the deposition.

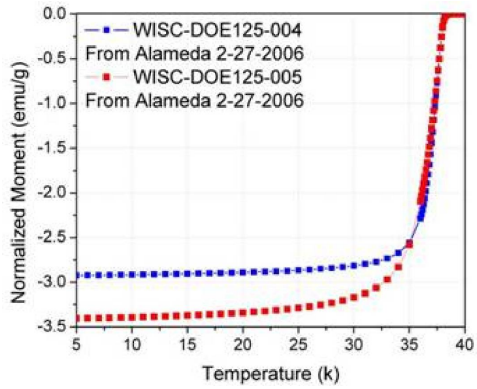

Figure 3: Superconducting transition in native sintered MgB_2 cathode.

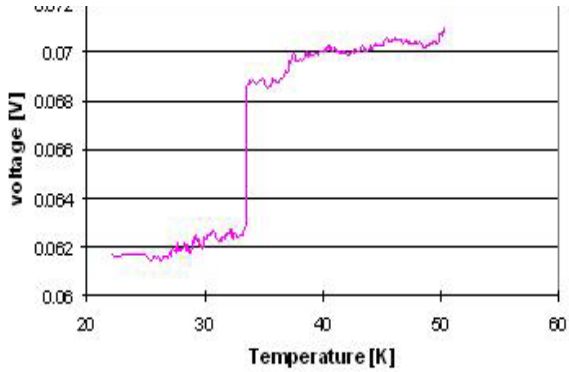

Figure 4: Superconducting transition (34K) in a 2µm, thick MgB film deposited on C-plane sapphire at 550K.

The films were shown to contain oxygen through both EDX and XPS analysis. Sufficient reduction of oxygen content was not possible within the present deposition sources, because a major oxygen source initially was the sintered cathode material itself. The density of sintered MgB_2 was significantly below the ideal value. The voids responsible for the reduced density can trap ambient gasses and the powdered precursor material that is sintered is known to contain an oxide skin. As shown in Fig. 5 (left), contamination (white MgO flakes) at the grain boundaries was present in the sintered MgB_2 cathode material despite the measured T_c of 38K.

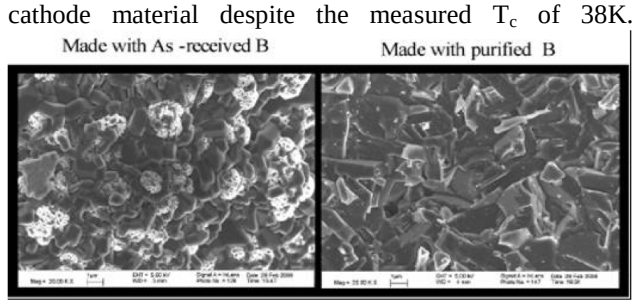

Figure 5: Comparison of MgB_2 material from traditional (left) and improved (right) sintering process.

The Applied Superconductivity Center at Florida State (ASC) has developed a new method to purify the cathode material prior to sintering (see Fig. 5 (right)) [15]

Superconductivity in Direct-deposited Films

With this improved target material, a new set of depositions was carried out in the direct deposition apparatus (Fig. 2). Several factors motivated the expectation of better results: (1) the purity of the raw MgB_2 target was superior to that used earlier with the CED™ apparatus; (2) the initial vacuum in the direct deposition apparatus was better (~10^{-9} Torr vs. ~10^{-8} Torr; (3) the rep-rate was higher, hence the interval between pulses was shorter and thus less oxygen contamination was expected between pulses from residual water vapor in the chamber.

However, the coated samples did not show superconducting transitions in the as-coated state! Possible reasons are offered in the discussion section later. The coated samples were annealed ex-situ and resistivity and SQUID measurements were performed for the annealed films. Figure 6 shows one such resistivity measurement and Fig. 7 the associated SQUID data.

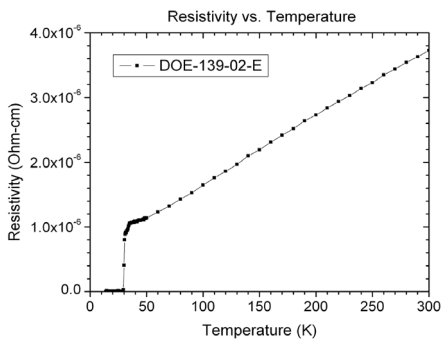

Figure 6: Resistivity vs. temperature of MgB_2 (after ex-situ annealing).

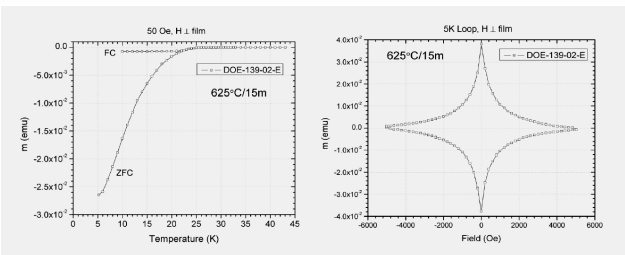

Figure 7: Resistivity vs. temperature of MgB_2 (after ex-situ annealing).

A T_c of approximately 30K is apparent from both the SQUID data in Fig. 7 (left) and the resistivity data in Fig. 8. Although this is below the ideal value of 39K, Fig. 7 (right) shows no offset in the peak of M indicating that the MgB_2 grains are well-connected with no MgO or other contaminants between the grains interrupting current flow. SEM imaging of the film surface after annealing revealed a dense, granular film that resembled high-quality bulk samples.

Even at the best deposition conditions, some authors claim that achieving a film T_c as high as the theoretical 39 K value may be impossible without a post-deposition anneal step. The annealing step is used to reorganize film atoms to create the correct crystal structure and reduce the internal energy in the film. Annealing is different from heating during deposition because there is no incident ion flux from the cathode so this heating does not affect the sticking coefficient. However above approximately 450°C magnesium evaporates from the film. For this reason precursor films that will undergo in situ anneal steps are often magnesium rich. For the CED™ process this can be readily achieved by depositing the pre-cursor film at a low temperature. Also temperature can vary throughout the pre-anneal deposition to create variations in the Mg to B ratio throughout the film thickness that can be designed in such a way as to counteract any variations caused by Mg depletion from the film surface during anneal. Most likely this will involve a Mg rich "cap" on a film that is itself somewhat enriched compared to MgB_2. Successful anneal steps spanning a wide range of heating/cooling times, temperatures and pressures are described in the literature.

Coating of RF Cavity Structures

A 2.2 GHz copper RF cavity half-cell was coated to demonstrate the feasibility of utilizing the CED™ process for this purpose. Figure 8 shows the coated half cell (left) together with an uncoated, identical half-cell (right) for comparison. No analysis was performed on the cavity to characterize the film. One observes that no un-coated regions or macroscopic defects are visible and the film appears well-adhered.

Figure 8: Copper RF cavity half-cell deposited using the CED™ process (left) and uncoated half-cell for comparison (right).

Along with Superconductivity characteristics such as T_c and RRR, there are mechanical characteristics necessary to producing a functional SRF cavity from MgB_2 coated Cu. Notably the film surface must be very smooth, with RMS roughness below approximately 150nm. SRF cavities drive large accelerating gradients as large as 200 MV/m. In these large electric fields, electron generation at the surface of the cavity is a formidable problem. Cathodic arc deposition methods such as CED™ produce macro-particles which are µm scale droplets of material produced from the cathode surface. At the cathode, arc current is focused into tiny (10-100µm^2), short lived (10ns-1µs) regions called cathode spots. Current densities in cathode spots are in excess of 1A/µm^2. Cathode material leaves the cathode spot as a mixture of plasma and macro-particles. The ratio of plasma to macro-particles is a strong function of the thermodynamic

properties of the cathode and the local current density. In the 1970's Daalder studied many cathode materials ranging from low melting point metals to refractory metals. The basic trend was that the fraction of the mass leaving the cathode as plasma increased with increased melting point of the cathode material. Daalder showed that the relative rate of macro-particle production (expressed as mass/coulomb) can be significantly reduced by reducing arc current. However it does so at the expense of deposition rate as less plasma is produced at lower arc currents. Thus a balance must be established between the large deposition rates desired to maintain low relative flux of impurities at the substrate surface and the low arc currents desired to reduce macro-particle production.

Likewise depositions can be performed at varying levels of applied axial B-field. It has been shown that increasing the cathode spot velocity causes a decrease in the production of macro-particles. Cathodic arc-spot velocity increases with increasing axial B-field.

DISCUSSION

Superconducting RF cavities enable research particle accelerators to achieve higher beam energies at lower operating powers. Superconducting cavities are made from niobium which is expensive and difficult to manufacture. Coating copper cavities with a thin film of a different superconductor with a higher transition temperature would save on both fabrication and operation costs and allow enhanced accelerator operation. This paper presents the first measurements of superconductivity in a thin-film of MgB_2 that was deposited in a single-step process using heated substrates and solid MgB_2 targets, in our CED™ energetic condensation apparatus. Subsequent depositions in our direct deposition apparatus, aimed at reducing oxygen contamination and starting with a higher purity (lower oxygen) MgB2 target, showed a surprising lack of superconductivity in the as-grown films. Only after ex-situ annealing did we see a transition, then too, at a lower temperature than had been measured in the CED™ coated samples. One possible reason for this is that the film might have been too thin. In the earlier CED™ films, it was observed that thicker films exhibit higher Tc and sharper transitions. This negative result highlights the complex interplay between grain structure, film thickness, deposition conditions, film stoichiometry and vacuum pre-bake conditions, in determining a good superconducting compound film such as MgB_2. Future work will further study the morphology of the film using SEM, EBSD, XRD and other tools, followed by RF tests in a superconducting impedance cavity (SIC) at Jlab.

ACKNOWLEDGMENTS

This research was supported by the US DOE via SBIR grants to AASC.

REFERENCES

[1] H. Padamsee, J. Knoblock, and T. Hays RF, Superconductivity for Accelerators John Wiley & Sons, Inc. 1998.

[2] T. Tajima, A. Canabal, Y. Zhao, A. Romanenko, C. Nantista, S. Tantawi, L. Phillips, Y. Iwashita, I. Campisi, and B. Moeckly. "TESTS ON MgB2 FOR APPLICATION TO SRF CAVITIES" Contributed to European Particle Accelerator Conference (EPAC 06), Edinburgh, Scotland, 26-30 Jun 2006.

[3] Benvenuti, C.; Bernard, P.; Bloess, D.; Cavallari, G.; Chiaveri, E.; Haebel, E.; Hilleret, N.; Tuckmantel, J.; Weingarten, W. In Superconducting niobium sputter-coated copper cavity modules for the LEP energy upgrade, New York, NY, USA, 1991; IEEE: New York, NY, USA, 1991; pp 1023-5.

[4] Benvenuti, C. Circelli, N.; Hauer, M., Niobium films for superconducting accelerating cavities. Applied Physics Letters 1984, 45, (5), 583-4.

[5] Calatroni, S., 20 Years of experience with the Nb/Cu technology for superconducting cavities and perspectives for future developments. Physica C 2006, 441, (1-2), 95-101

[6] Russo, R., Quality measurement of niobium thin films for Nb/Cu Superconducting RF cavities. Meas. Sci. Techno. 2007, 18, 2299-2313.

[7] A-M. Valente-Feliciano. "Overview: New Materials for SRF Cavities" Presentation to SRF Materials Workshop, May 23-24 2007.

[8] R.G. Sharma. "A Review on A-15 Superconductors for RF Cavity Applications", contributed to the International Workshop on: Thin Films and New Ideas for Pushing the Limits of RF Superconductivity, October 9-12 2006, INFN Italy.

[9] E. Hand, Nature, Vol 456|4 December 2008 p555.

[10] J. Nagamatsu, N Nakagawa, T. Muranaka, Y. Zenitani and J. Akimitsu "Superconductivity at 39 K in magnesium diboride" *NATURE* VOL 410 1 MARCH 2001 pp 63-64.

[11] B, G. Catelani and J. P. Sethna, http://arXiv.org/abs/0810.4720; 2008.

[12] X.X. Xi, A.V. Pogrebnyakov, X.H. Zeng, J.M. Redwing, S Y Xu, Qi Li, Zi-Kui Liu, J Lettieri, V Vaithyanathan, DG Schlom, H M Christen, H Y Zhai and A Goyal "Progress in the deposition of MgB2 thin films" Supercond. Sci. Technol. 17 (2004) S196–S201.

[13] P. Badica, K. Togano, S. Awaji and K. Watanabe. Supercond. Sci. Technol. 19 (2006) 242–246

[14] X. L Wang Q. W. Yao, J. Horvat M. J. Qin and S. X. Dou, Supercond. Sci. Technol. 17 No 3 (March 2004) L21-L24.

[15] Jiang J, Senkowicz B J, Larbalestier D C, and Hellstrom E E, SUPERCONDUCTOR SCIENCE & TECHNOLOGY,Vol.19, ppL33-L36 (2006).